

# QUINOXALINE-CONTAINING AB<sub>2</sub> MONOMER FOR HYPERBRANCHED AROMATIC POLY(ETHER-KETONES)

## CROSS REFERENCE TO RELATED APPLICATION

5        This application claims priority of the filing date of Provisional Application serial  
number 60/453,333, filed 02-28-2003.

## RIGHTS OF THE GOVERNMENT

      The invention described herein may be manufactured and used by or for the  
Government of the United States for all governmental purposes without the payment of  
10    any royalty.

## BACKGROUND OF THE INVENTION

      The present invention relates to a new quinoxaline-containing AB<sub>2</sub> monomer that  
is useful for the preparation of hyperbranched poly(ether-ketones).

      Dendritic macromolecules such as dendrimers and hyperbranched polymers are  
15    a new class of highly branched polymers that have distinctly different properties from  
their linear analogs. Both dendrimers and hyperbranched polymers have much lower  
solution and melt viscosities than their linear analogs of similar molecular weights. They  
also have a large number of chain-ends whose collective influence dictates their overall  
physical and/or chemical behaviors. These features are attractive in terms of  
20    processability and offering flexibility in engineering required properties for specific  
applications. However, there is a practical advantage that hyperbranched polymers  
have over dendrimers at "raw material" level. Although dendrimers have precisely  
controlled structures (designated as generations), their preparations generally involve  
tedious, multi-step sequences that are impractical and costly in scale-up production.  
25    Synthesis of a hyperbranched polymer, on the other hand, is a one-pot process. Large

quantities of hyperbranched polymers can be easily produced from  $AB_x$  ( $x \geq 2$ ) monomers.

Because of their excellent thermal and mechanical properties, as well as their optical and electronic characteristics, aromatic, fused heterocyclic polymers such as polyquinoxalines and polybenzoxazoles continue to attract considerable attention. However, they have limited processability due to the nature of fused ring systems. Their insolubility and their softening temperatures are generally above their degradation temperatures. Chemical modification on these materials, for example, by the use of solubilizing pendants or flexible units in the main chain, has been successful to improve their processability, allowing the optimization of their properties as a function of processability. Another viable approach to achieving this objective is to incorporate the elements of local rigidity and global randomness into the macromolecular architecture. Local rigidity provides the thermal, electronic and optical characteristics of the aromatic fused systems while global randomness frustrates entanglement of the polymer chains, leading to greater solubility. Dendritic structures clearly embody these qualities. However, as noted previously, hyperbranched structures have greater synthetic practicality.

Accordingly, it is an object of the present invention to provide a novel quinoxaline-containing  $AB_2$  monomer that is useful for the preparation of hyperbranched poly(ether-ketones).

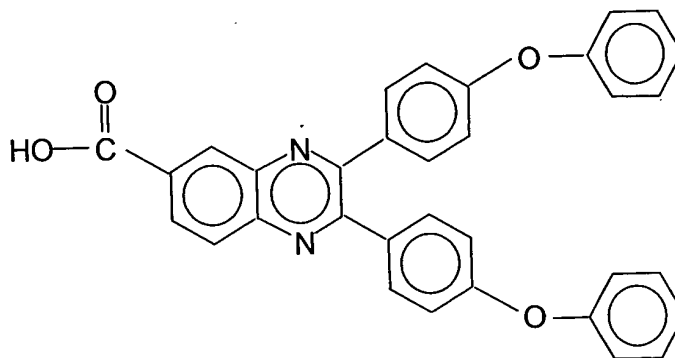
Other objects and advantages of the invention will be set forth in part in the description which follows, and in part will be obvious from the description, or may be learned by practice of the invention. The objects and advantages of the invention may

be realized and attained by means of the instrumentalities and combinations particularly pointed out in the appended claims.

### SUMMARY OF THE INVENTION

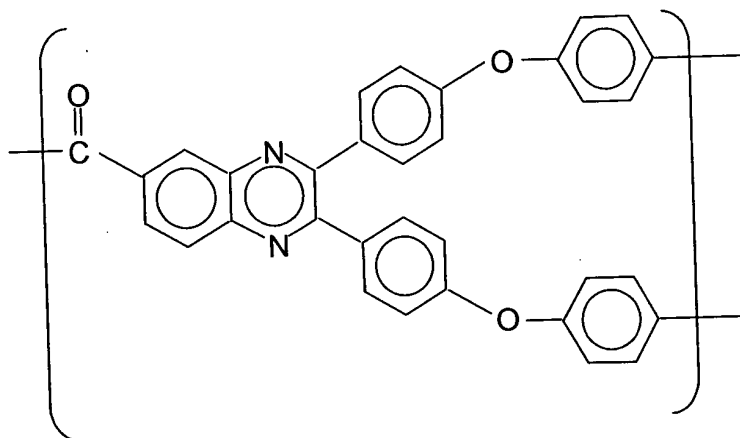
In accordance with the present invention there is provided a novel AB<sub>2</sub> monomer,

5 2,3-bis(4-phenyloxyphenyl)-6-quinoxaline carboxylic acid, having the formula:



The AB<sub>2</sub> monomer, 2,3-bis(4-phenyloxyphenyl)-6-quinoxaline carboxylic acid, is synthesized as set forth in the examples which follow.

The AB<sub>2</sub> monomer, 2,3-bis(4-phenyloxyphenyl)-6-quinoxaline carboxylic acid, is  
10 useful for preparing the hyperbranched ether-ketone polymer:



The following examples illustrate the invention:

#### Example 1

##### 1-(2-Methyl-3-butyn-2-ol)-2-(4-phenyloxyphenyl)ethyne

Into a 1 L three-necked, round-bottomed flask equipped with a magnetic stirrer, a  
 5 condenser, and a nitrogen inlet, 4-bromodiphenylether (50.1g, 201 mmol), freshly  
 distilled 2-methyl-3-butyn-2-ol (64.3g, 892 mmol), copper(I) iodide (0.11g, 0.60 mmol),  
 triphenylphosphine (0.33g, 1.3 mmol), and bis(triphenylphosphine)palladium(II) chloride  
 (1.12g, 1.6 mmol) were placed. The solids were carefully washed in with triethylamine  
 (500 mL). The mixture was heated under reflux for 24h. After the reaction mixture had  
 10 been allowed to cool to room temperature, the solution was filtered through silica gel.  
 The filtrate was poured into 5% hydrochloric acid solution and diluted with methylene  
 chloride. After separation from the aqueous phase, the organic phase was subjected to  
 purification via a silica-gel column chromatography with methylene chloride/hexane  
 elution to give 40.5g (80% yield) of light yellow oil. Anal. Calcd. for  $C_{17}H_{16}O_2$ : C,  
 15 80.93%; H, 6.39%; O, 12.68%. Found: C, 80.88%; H, 6.43%; O, 12.89%. Mass  
 spectrum (m/e): 252 ( $M^+$ , 100% relative abundance).

#### Example 2

##### (4-Phenyloxyphenyl)ethyne

Into a 1 L three-necked, round-bottomed flask equipped with a magnetic stirrer, a  
 20 condenser, and a nitrogen inlet, 1-(2-methyl-3-butyn-2-ol)-2-(4-phenyloxyphenyl)ethyne  
 (40.0g, 159 mmol) was dissolved in toluene (700 mL). A solution of potassium  
 hydroxide (2.2g, 39.2 mmol) in methanol (40 mL) was added. The mixture was heated  
 under reflux 14h. The solution was concentrated to approximately 100 mL and then

purified by silica-gel column chromatography with pentane elution to give 28.0g (90% yield) of light yellow oil. Anal. Calcd. for  $C_{14}H_{10}O$ : C, 86.57%; H, 5.19%; O, 8.24%. Found: C, 86.52%; H, 5.25%; O, 8.29%. Mass spectrum (m/e): 194 ( $M^+$ , 100% relative abundance).

### Example 3

#### 1,2-Bis(4-phenyloxyphenyl)ethyne

Into a 1 L three-necked round-bottomed flask equipped with a magnetic stirrer, a condenser, and a nitrogen inlet, (4-phenyloxyphenyl)ethyne (28.0g, 144 mmol), 4-bromodiphenylether (27.7g, 151 mmol), copper(I) iodide (0.10g, 0.53 mmol), triphenylphosphine (0.30g, 1.1 mmol), and bis(triphenylphosphine)palladium(II) chloride (1.00g, 1.4 mmol) were placed. The solids were carefully washed in with triethylamine (500 mL). The mixture was then heated under reflux for 24h. After the reaction mixture had been allowed to cool to room temperature, the solution was filtered through silica gel. The filtrate was poured into 5% hydrochloric acid solution and diluted with methylene chloride. After separation from the aqueous phase, the organic phase was subjected to a silica-gel column chromatography with petroleum ether elution to remove the excess 4-bromodiphenylether and then methylene chloride/hexane (33/67, v/v) elution to give 42.3g (81% yield) of white crystals. It was again recrystallized from toluene to give 32.1g (62% yield) of white flakes, m.p. 173-174°C. Anal. Calcd. for  $C_{26}H_{18}O_2$ : C, 86.17%; H, 5.01%; O, 8.83%. Found: C, 86.13%; H, 5.40%; O, 8.43%. FT-IR (KBr,  $cm^{-1}$ ): 738, 3039, 3061. Mass spectrum (m/e): 362 ( $M^+$ , 100% relative abundance).  $^1H$  NMR (DMSO- $d_6$ , ppm)  $\delta$  6.97-7.00 (dd, 4H, Ar), 7.04-7.08 (m, 4H, Ar), 7.15-7.21 (t, 2H, Ar), 7.38-7.44 (t, 4H, Ar), 7.49-7.52 (d, 4H, Ar).

## Example 4

## 1,2-Bis(4-phenyloxyphenyl)benzil

(Method 1) Into a 1 L three-necked round-bottomed flask equipped with a magnetic stirrer, a condenser, a dropping funnel and a nitrogen inlet, 1,2-bis(4-phenyloxyphenyl)ethyne (4.0g, 11.0 mmol) and methyltrialkyl ammonium chlorides (Adogen 454, 1.25g) were dissolved in methylene chloride (200 mL). A solution of potassium permanganate (16.0g, 101 mmol) in acetic acid (30 mL) and water (500 mL) was slowly added through a dropping funnel. The mixture was gently heated under reflux for 10h. After cooling down to room temperature, the mixture was poured in large flask, potassium bisulfate was added until the mixture became clear, and then a small amount of sodium bicarbonate was added. The organic layer was then separated, dried over magnesium sulfate, filtered, and solvent was removed under the reduced pressure to give 4.22g of light yellow solid, which was re-dissolved in hot ethanol or heptane and allowed to cool to room temperature to give 3.88g (89% yield) of light yellow powder, m.p.119-120°C. Anal. Calcd. for  $C_{26}H_{18}O_4$ : C, 79.17%; H, 4.60%. Found: C, 79.83%; H, 4.89%. FT-IR (KBr,  $cm^{-1}$ ): 1667. Mass spectrum (m/e): 394 ( $M^+$ , 100% relative abundance).  $^1H$  NMR (DMSO- $d_6$ , ppm)  $\delta$  7.00 -7.06 (dd, 4H, Ar), 7.06-7.11 (m, 4H, Ar), 7.20-7.25 (t, 2H, Ar), 7.37-7.44 (t, 4H, Ar), 7.78-7.96(dd, 4H, Ar).  $^{13}C$  NMR (DMSO- $d_6$ , ppm)  $\delta$  117.44, 120.46, 125.06, 127.51, 130.16, 132.20, 154.84, 155.89, 162.35, 163.56.

(Method 2). Into a 250 mL three-necked, round-bottomed flask equipped with a magnetic stirrer, a condenser, a dropping funnel and a nitrogen inlet, phenol (8.0g, 85.0 mmol) and potassium carbonate (13.5g, 98 mmol) were dispersed in NMP (100 mL).

Then, the mixture was heated at 150°C overnight. After the reaction mixture had been allowed to cool to 130°C, a solution of 4,4'-difluorobenzil (10.0g, 40.6 mmol) in NMP (50 mL) was slowly added through the dropping funnel. The mixture was heated at 145°C for 10h. Upon cooling down to room temperature, the mixture was filtered and the  
 5 filtrate was poured into 5% hydrochloric acid. The resulting precipitate was collected, air-dried, and dissolved in hot ethanol or heptane and allowed to cool to room temperature to give 13.6g (85% yield) of light yellow powder: m.p. 120-122°C. Anal. Calcd. for C<sub>26</sub>H<sub>18</sub>O<sub>4</sub>: C, 79.17%; H, 4.60%. Found: C, 79.19%; H, 4.75%. FT-IR (KBr, cm<sup>-1</sup>): 1666. Mass spectrum (m/e): 394 (M<sup>+</sup>, 100% relative abundance). <sup>1</sup>H NMR  
 10 (DMSO-d<sub>6</sub>, ppm) δ 7.01 -7.05 (dd, 4H, Ar), 7.05-7.10 (m, 4H, Ar), 7.19-7.26 (t, 2H, Ar), 7.36-7.44 (t, 4H, Ar), 7.78-7.95(dd, 4H, Ar). <sup>13</sup>C NMR (DMSO-d<sub>6</sub>, ppm) δ 117.43, 120.45, 125.06, 127.50, 130.15, 132.20, 154.83, 155.88, 162.33, 163.55.

### Example 5

#### 2,3-Bis(4-phenyloxyphenyl)-6-quinoxaline-carboxylic acid

15 Into a 250 mL three-necked, round-bottomed flask equipped with a magnetic stirrer, a condenser, and a nitrogen inlet, 3,4-diaminobenzoic acid (2.65 g, 17.4 mmol) was dissolved in acetic acid (150 mL). 4,4'-Diphenyloxybenzil (6.55 g, 16.6 mmol) was then added and heated under reflux for 12h. Upon cooling to room temperature, the resulting dark red solution was filtered and the filtrate was poured into 5% hydrochloric  
 20 acid. The resulting light yellow precipitate was collected by suction filtration and air-dried. It was recrystallized from ethanol to give 7.0 g (83% yield) of bright yellow powder: m.p. 224-226°C. Anal. Calcd. for C<sub>33</sub>H<sub>22</sub>N<sub>2</sub>O<sub>4</sub>: C, 77.63%; H, 4.34%; N, 5.49%; O, 12.54%. Found: C, 77.71%; H, 4.39%; N, 5.27%; O, 12.41%: FT-IR (KBr, cm<sup>-1</sup>):

1242, 1488, 1588, 1697. Mass spectrum (m/e): 510 ( $M^+$ , 100% relative abundance).  $^1\text{H}$  NMR (DMSO- $d_6$ , ppm)  $\delta$  6.99-7.02 (d, 4H, Ar), 7.06-7.09 (d, 4H, Ar), 7.14-7.25 (m, 2H, Ar), 7.39-7.45 (t, 4H, Ar), 7.52-7.55(d, 4H, Ar), 8.14-8.17 (d, 1H, Ar), 8.26-8.29 (dd, 1H, Ar), 8.61-8.62 (d, 1H, Ar).  $^{13}\text{C}$  NMR (DMSO- $d_6$ , ppm)  $\delta$  117.00, 117.66, 119.08, 119.91, 5 123.91, 129.01, 129.99, 130.08, 130.25, 131.57, 131.66, 131.83, 132.03, 133.13, 139.52, 142.17, 153.23, 153.83, 154.93, 155.79, 155.85, 157.55, 157.66, 160.69, 166.53.

Having thus described exemplary embodiments of the present invention, it should be noted by those skilled in the art that the disclosures herein are exemplary 10 only and that alternatives, adaptations and modifications may be made within the scope of the present invention.